



# Chemical Translations



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## CERTIFICATE OF ACCURACY

State of New York

} ss.

County of Erie

German

TRANSLATION FROM \_\_\_\_\_

On this day, I **S. Edmund Berger** state:

German

that I am a professional translator of the \_\_\_\_\_ and English languages,  
doing business as *Chemical Translations*, 298 Grayton Road, Tonawanda, NY 14150;

that I am thoroughly familiar with these languages and have carefully made and/or verified the  
attached translation from the original document

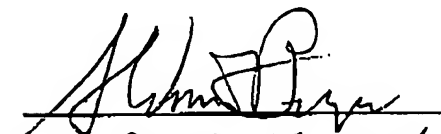
NEW US PCT PATENT APPLICATION  
PCT/EP 2004/012941  
Inv.: PASQUIER, C., ET AL.  
SER. NO.: 10/563,354  
Ref. 3644

as submitted to me in the

German

\_\_\_\_\_ language;

and that the said translation is a true, complete and correct English version of such original to the  
best of my knowledge and belief.

  
April 19, 2006

## DESCRIPTION

**Agent and Method for the Oxidative Coloring of Keratin Fibers**

5

The present application has for an object a ready-to-use agent for coloring keratin fibers, for example silk, wool or hair and particularly human hair, said agent containing (i) a heterocyclic hydrazone derivative, (ii) a -CH-active compound and (iii) an oxidant and furthermore a multicomponent kit and a method for coloring keratin fibers by use of said colorant.

10

Hair colorants are divided mainly into the groups of oxidation colorants and tinting agents, depending on the starting hair to be colored and the desired result. Oxidation colorants are eminently suited for covering large gray areas, the oxidation colorants used for gray areas of up to 50% are usually referred to as oxidative tinting agents, whereas the oxidation colorants used for gray areas of more than 50% or for "brightening" are usually referred to as oxidative colorants. Direct dyes are contained primarily in non-oxidative colorants (tinting agents). Because of their small molecular size, some direct dyes, for example nitro dyes, can penetrate into the hair and dye it directly, at least in the outer regions. Such tinting is very gentle to the hair and as a rule can withstand 6 to 8 hair washings. Direct dyes are frequently used also in oxidative colorants for producing certain shades or to intensify the color.

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DE-A 1 922 400 discloses the use of hydrazones for coloring keratin fibers. These colorants, however, cannot meet the requirements placed on colorants in every respect, particularly as regards the luster and intensity of the colorations.

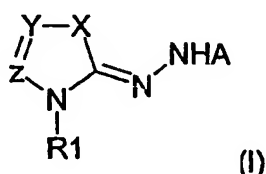
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Surprisingly, we have now found that intense and bright colorations are obtained by use of a combination of certain heterocyclic hydrazones and certain CH-active compounds in the presence of an oxidant.

30

Hence, the present invention has for an object a ready-to-use agent for coloring keratin fibers, for example wool, silk or hair and particularly human hair, characterized in that it contains

(a) at least one hydrazone derivative of formula (I) or a physiologically compatible salt thereof:



wherein

**X** stands for oxygen, sulfur or NR<sub>2</sub>,

10 **Y** stands for C-R<sub>3</sub> or nitrogen and

**Z** stands for C-R<sub>4</sub> or nitrogen,

provided that the heterocyclic part of the compound of formula (I) contains at the most three heteroatoms;

15 **A** stands for hydrogen, an acetyl group, a trifluoroacetyl group, a formyl group, a (C<sub>1</sub>-C<sub>6</sub>)-alkylsulfonyl group or an arylsulfonyl group;

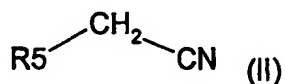
R<sub>1</sub> and R<sub>2</sub> can be equal or different and independently of each other denote a saturated or unsaturated (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a halogen (F, Cl, Br, I)-substituted (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a hydroxy-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, an amino-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a sulfonic acid-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a formyl group, a -C(CO)-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a substituted or unsubstituted -C(O)-phenyl group, a -C(O)NH-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a substituted or unsubstituted -C(O)NH-phenyl group, a substituted or unsubstituted phenyl group or a benzyl group;

25 **R<sub>3</sub>** and **R<sub>4</sub>** can be identical or different and independently of each other denote hydrogen, a halogen atom (F, Cl, Br, I), a saturated or unsaturated (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a halogen atom (F, Cl, Br, I)-substituted (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a hydroxy-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a (C<sub>1</sub>-C<sub>12</sub>)-alkoxy group, a cyano group, a nitro group, an amino group, a (C<sub>1</sub>-C<sub>12</sub>)-alkylamino group, a di(C<sub>1</sub>-C<sub>12</sub>)-alkylamino group, a carboxyl group, a -C(O)O-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a substituted or unsubstituted -C(O)O-phenyl group, a substituted or unsubstituted phenyl

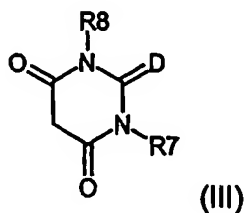
phenyl group or a naphthyl group;

and when **Y** and **Z** stand for C-R3 and C-R4, **R3** and **R4** together with the remainder of the molecule can form a heterocyclic or carbocyclic, saturated or unsaturated, substituted or unsubstituted ring system;

- 5 (b) at least one CH-active compound of formulas (II) to (IX) with

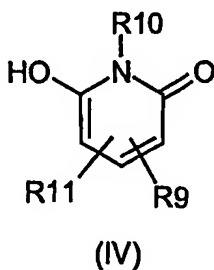


- wherein **R5** denotes a cyano group, a (CO)-R6 carbonyl function, with **R6** denoting a (C<sub>1</sub>-C<sub>12</sub>)-alkoxy group, an amino group, a (C<sub>1</sub>-C<sub>12</sub>)-alkylamino group, an arylamino group, (C<sub>1</sub>-C<sub>12</sub>)-alkyl group or an aryl group;
- 10



- wherein **R7** and **R8** can be equal or different and denote hydrogen, a (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a monohydroxy-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a polyhydroxy-(C<sub>2</sub>-C<sub>12</sub>)-alkyl group, a mono-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>1</sub>-C<sub>6</sub>)-alkyl group, a poly-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>2</sub>-C<sub>6</sub>)-alkyl group, an amino-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, or a carbocyclic or heterocyclic, substituted or unsubstituted aromatic compound,
- 15

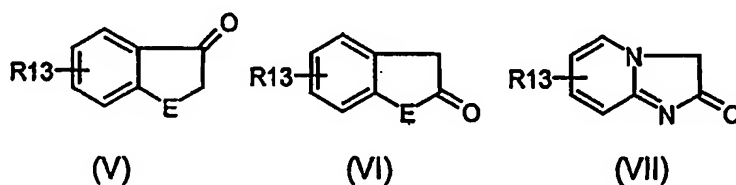
and **D** stands for a sulfur atom or oxygen atom;



- 20 wherein **R9** denotes a hydrogen atom, a nitrile group, a (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a carbocyclic

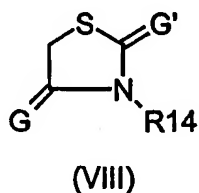
or heterocyclic aromatic compound or a (CO)-R12 carbonyl function, within **R12** standing for hydrogen, a hydroxyl group, a (C<sub>1</sub>-C<sub>12</sub>)-alkoxy group, an amino group, a (C<sub>1</sub>-C<sub>12</sub>)-alkylamino group, a (C<sub>1</sub>-C<sub>12</sub>)-alkyl group or an aryl group, and

**R10** and **R11** can be equal or different and independently of each other denote hydrogen, a (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a monohydroxy-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a polyhydroxy-(C<sub>2</sub>-C<sub>12</sub>)-alkyl group, a mono-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>1</sub>-C<sub>6</sub>)-alkyl group, a poly-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>2</sub>-C<sub>6</sub>)-alkyl group, an amino-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, or a carbocyclic or heterocyclic aromatic compound;



wherein **E** denotes an oxygen atom, a sulfur atom of an NR' amino group, with R' standing for hydrogen or a substituted or unsubstituted (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, and

**R13** stands for a hydrogen atom, a halogen atom (Cl, Br, I, F), a hydroxyl group, a cyano group, a nitro group, a (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a monohydroxy-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a polyhydroxy-(C<sub>2</sub>-C<sub>12</sub>)-alkyl group, a mono-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>1</sub>-C<sub>6</sub>)-alkyl group, a poly-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>1</sub>-C<sub>6</sub>)-alkyl group, an amino-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, or a carbocyclic or heterocyclic aromatic compound, a carboxamide or a sulfonamide;

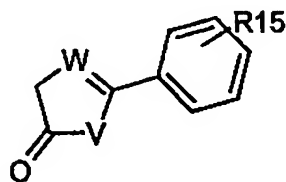


wherein **G** and **G'** can be equal or different and independently of each other denote an oxygen atom, a sulfur atom or an NR'' amino group, with R'' standing for hydrogen or a substituted or

unsubstituted (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, and

**R14** denotes hydrogen, a substituted or unsubstituted (C<sub>1</sub>-C<sub>12</sub>)-alkyl group or a carbocyclic

or heterocyclic, substituted or unsubstituted aromatic compound;



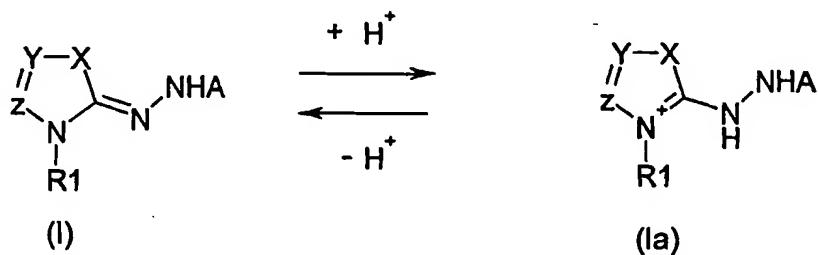
(IX)

wherein **V** stands for an oxygen atom or an NR<sup>'''</sup> amino group, with R<sup>'''</sup> denoting hydrogen, or a substituted or unsubstituted (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, and

- 5 **R<sub>15</sub>** stands for a hydrogen atom, a halogen atom, a hydroxyl group, a cyano, a nitro group, a (C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a monohydroxy-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a polyhydroxy-(C<sub>2</sub>-C<sub>12</sub>)-alkyl group, a mono-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>1</sub>-C<sub>6</sub>)-alkyl group, a poly-(C<sub>1</sub>-C<sub>6</sub>)-alkoxy-(C<sub>1</sub>-C<sub>6</sub>)-alkyl group, an amino-(C<sub>1</sub>-C<sub>12</sub>)-alkyl group, a carbocyclic or heterocyclic aromatic compound, a carboxamide or a sulfonamide;

- 10 and (c) at least one oxidant.

Depending on the pH of the agent, the compound of formula (I) can also be in equilibrium with the compound of formula (Ia):



- 15 Preferred hydrazones are hydrazone derivatives of formula (I) or the physiologically compatible salts thereof wherein:

(i) **X** denotes a sulfur atom, **Y** denotes C-R<sub>3</sub>, **Z** denotes C-R<sub>4</sub> and **A** stands for a hydrogen atom, or

(ii) **X** denotes N-R<sub>2</sub>, **Y** denotes nitrogen and **A** stands for a hydrogen atom;

- 20 the hydrazone derivatives of formula (I) or the physiologically compatible salts thereof wherein **X** denotes sulfur, **Y** denotes C-R<sub>3</sub>, **Z** denotes C-R<sub>4</sub> and **A** stands for hydrogen

being particularly preferred.

Examples of compounds of formula (I) are the following as well as the salts thereof:

- 3-methyl-2(3H)-thiazolone hydrazone,
- 5 3,4-dimethyl-2(3H)-thiazolone hydrazone,
- 4-tert.butyl-3-methyl-2(3H)-thiazolone hydrazone,
- 3-methyl-4-phenyl-2(3H)-thiazolone hydrazone,
- 3-methyl-4-(4-tolyl)-2(3H)-thiazolone hydrazone,
- 4-(4-methoxy)phenyl-3-methyl-2(3H)-thiazolone hydrazone,
- 10 4-(4-ethoxy)phenyl-3-methyl-2(3H)-thiazolone hydrazone,
- 4-(4-bromophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
- 4-(3-bromophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
- 4-(4-chlorophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
- 4-(3-chlorophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
- 15 3-methyl-4-(4-nitrophenyl)-2(3H)-thiazolone hydrazone,
- 3-methyl-4-(3-nitrophenyl)-2(3H)-thiazolone hydrazone,
- 4-[(1,1'-biphenyl)-4-yl]-3-methyl-2(3H)-thiazolone hydrazone,
- 3-methyl-4-(2-naphthalenyl)-2(3H)-thiazolone hydrazone,
- ethyl 2-hydrazono-2,3-dihydro-3-methyl-4-thiazolecarboxylate,
- 20 3,4,5-trimethyl-2(3H)-thiazolone hydrazone,
- 3,4-dimethyl-5-phenyl-2(3H)-thiazolone hydrazone,
- 3,5-dimethyl-4-phenyl-2(3H)-thiazolone hydrazone,
- 4,5-diphenyl-3-methyl-2(3H)-thiazolone hydrazone,
- 5-ethyl-3-methyl-4-phenyl-2(3H)-thiazolone hydrazone,
- 25 4-(4-bromophenyl)-3-methyl-5-phenyl-2(3H)-thiazolone hydrazone,
- 3-methyl-5-phenyl-4-(4-tolyl)-2(3H)-thiazolone hydrazone,
- 5-(4-chlorophenyl)-4-phenyl-3-methyl-2(3H)-thiazolone hydrazone,
- 5-(4-chlorophenyl)-4-(4-methoxyphenyl)-3-methyl-2(3H)-thiazolone hydrazone,
- ethyl 2-hydrazono-2,3-dihydro-3,4-dimethyl-4-thiazolecarboxylate,
- 30 4-amino-2-hydrazono-2,3-dihydro-3-methyl-5-thiazole carbonitrile

4,5-dimethyl-3-ethyl-2(3H)-thiazolone hydrazone,  
 ethyl 2-hydrazono-2,3-dihydro-3-ethyl-4-methylthiazolecarboxylate,  
 5-methyl-3-(1-methylethyl)-4-phenyl-2(3H)-thiazolone hydrazone,  
 3-(1-methylethyl)-4,5-diphenyl-2(3H)-thiazolone hydrazone,  
 5 4,5-diphenyl-3-propyl-2(3H)-thiazolone hydrazone,  
 3-butyl-4,5-diphenyl-2(3H)-thiazolone hydrazone,  
 4,5-diphenyl-3-(2-methylpropyl)-2(3H)-thiazolone hydrazone,  
 3-hydroxyethyl-2(3H)-thiazolone hydrazone,  
 3-hydroxyethyl-4-methyl-2(3H)-thiazolone hydrazone,  
 10 3-aminoethyl-2(3H)-thiazolone hydrazone,  
 3-aminoethyl-4-methyl-2(3H)-thiazolone hydrazone,  
 3,4-diphenyl-2(3H)-thiazolone hydrazone,  
 4-methyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 4-p-biphenyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 15 4-(4-methoxy)phenyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 4-tert.butyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 3,4-diphenyl-5-methyl-2(3H)-thiazolone hydrazone,  
 3,4,5-triphenyl-2(3H)-thiazolone hydrazone,  
 4,5-dimethyl-3-(phenylmethyl)-2(3H)-thiazolone hydrazone,  
 20 3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4-methyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4-tert.butyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4-phenyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4,5-diphenyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 25 ethyl 2-hydrazono-2,3-dihydro-3-[(phenylamino)carbonyl]-4-methylthiazolecarboxylate  
 3-methyl-4,5,6,7-tetrahydro-2(3H)-benzothiazolone hydrazone,  
 3-methyl-2(3H)benzothiazolone hydrazone,  
 3,6-dimethyl-2(3H)benzothiazolone hydrazone,  
 6-chloro-3-methyl-2(3H)benzothiazolone hydrazone,  
 30 7-chloro-3-methyl-2(3H)benzothiazolone hydrazone,



6-hydroxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 5-methoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 7-methoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 5,6-dimethoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 5 5-ethoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 6-ethoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 3-methyl-5-nitro-2(3H)benzothiazolone hydrazone,  
 3-methyl-6-nitro-2(3H)benzothiazolone hydrazone,  
 5-acetamido-3-methyl-2(3H)benzothiazolone hydrazone,  
 10 6-acetamido-3-methyl-2(3H)benzothiazolone hydrazone,  
 5-anilino-3-methyl-2(3H)benzothiazolone hydrazone,  
 6-anilino-3-methyl-2(3H)benzothiazolone hydrazone,  
 2-hydrazono-2,3-dihydro-3-methyl-6-benzothiazolecarboxylic acid,  
 2-hydrazono-2,3-dihydro-3-methyl-4-benzothiazolesulfonic acid,  
 15 2-hydrazono-2,3-dihydro-3-methyl-5-benzothiazolesulfonic acid,  
 2-hydrazono-2,3-dihydro-3-methyl-6-benzothiazolesulfonic acid,  
 2-hydrazono-2,3-dihydro-3-methyl-7-benzothiazolesulfonic acid,  
 2-hydrazono-2,3-dihydro-N,N,3-trimethyl-6-benzothiazolesulfonamide,  
 [(2-hydrazono-2,3-dihydro-3-methyl-6-benzothiazolyl)oxy]acetic acid hydrazide,  
 20 (3-methylnaphtho[2,3-d]thiazole-2(3H)one hydrazone,  
 3-ethyl-2(3H)benzothiazolone hydrazone,  
 6-ethoxy-3-ethyl-2(3H)benzothiazolone hydrazone,  
 3-propyl-2(3H)benzothiazolone hydrazone,  
 3-butyl-2(3H)benzothiazolone hydrazone,  
 25 3-hexyl-2(3H)benzothiazolone hydrazone,  
 3-hydroxyethyl-2(3H)benzothiazolone hydrazone,  
 3-aminoethyl-2(3H)benzothiazolone hydrazone,  
 3-p-methylbenzyl-2(3H)benzothiazolone hydrazone,  
 2-hydrazono-2,3-dihydro-3-(2-hydroxyethyl)-6-benzothiazolecarboxylic acid,  
 30 2-hydrazono-2,3-dihydro-6-methoxy-3(2H)benzothiazolepropanesulfonic acid,

6-hexadecyloxy-2-hydrazono-3(2H)benzothiazolepropanesulfonic acid,  
 ethyl 2-keto-3-benzothiazoline acetate hydrazone,  
 3-acetyl-2(3H)-benzothiazolone hydrazone,  
 2-hydrazono-3(2H)benzothiazole carboxaldehyde,  
 5 3-methyl-2(3H)oxazolone hydrazone,  
 3-phenyl-2(3H)oxazolone hydrazone,  
 3-methyl-2(3H)benzoxazolone hydrazone,  
 3-phenyl-2(3H)benzoxazolone hydrazone,  
 1,3-dimethyl-4-imidazolin-2-one hydrazone,  
 10 1,3-diethyl-4-imidazolin-2-one hydrazone,  
 1,3-dihydroxyethyl-4-imidazolin-2-one hydrazone,  
 1,3-diaminoethyl-4-imidazolin-2-one hydrazone,  
 1,3-dimethyl-4-methoxy-4-imidazolin-2-one hydrazone,  
 1,3,4-trimethyl-4-imidazolin-2-one hydrazone,  
 15 1,3-dimethyl-4-phenyl-4-imidazolin-2-one hydrazone,  
 4-carboxy-1,3-dimethyl-4-imidazolin-2-one hydrazone,  
 4-amino-1,3-dimethyl-4-imidazolin-2-one hydrazone,  
 1,3-dimethyl-4-dimethylamino-4-imidazolin-2-one hydrazone,  
 1,3-dimethyl-2-benzimidazolinone hydrazone,  
 20 1,3-diethyl-2-benzimidazolinone hydrazone,  
 1,3-dihydroxyethyl-2-benzimidazolinone hydrazone,  
 1,3-diaminoethyl-2-benzimidazolinone hydrazone,  
 1,3,5-trimethyl-2-benzimidazolinone hydrazone,  
 5-methoxy-1,3-dimethyl-2-benzimidazolinone hydrazone,  
 25 5-bromo-1,3-dimethyl-2-benzimidazolinone hydrazone,  
 4,6-dibromo-1,3-dimethyl-2-benzimidazolinone hydrazone,  
 5-chloro-1,3-dimethyl-2-benzimidazolinone hydrazone,  
 1,3-dimethyl-5-nitro-2-benzimidazolinone hydrazone,  
 1,3-dimethyl-6-nitro-2-benzimidazolinone hydrazone,  
 30 1,4-dimethyl- $\Delta^2$ -1,2,4-triazoline-5-one hydrazone,

1,4-dihydroxyethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 1,4-diaminoethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 1,3,4-trimethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 1,4-dimethyl-3-phenyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 5 1,4-dimethyl-3-methoxy- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 1,4-dimethyl-3-dimethylamino- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 4-carboxy-1,4-dimethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 4-amino-1,4-dimethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 4-butyl-1-methyl-3-phenyl- $\Delta$ 2-1,3,4-triazoline-5-one hydrazone,  
 10 4-methyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 4-hydroxyethyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 4-aminoethyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 4-methyl-2-phenyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 2-methoxy-4-methyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 15 2-anilino-4-methyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 2-amino-4-methyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 2-dimethylamino-4-methyl- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 4-methyl-2-(methylthio)- $\Delta$ 2-1,3,4-thiadiazoline-5-one hydrazone,  
 4-(5-hydrazono-4,5-dihydro-4-methyl-1,3,4-thiadiazol-2-yl)benzenesulfonyl fluoride,  
 20 4-methyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 4-hydroxyethyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 4-aminoethyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 4-methyl-3-phenyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 3-methoxy-4-methyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 25 3-amino-4-methyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 3-dimethylamino-4-methyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 3-carboxy-4-methyl- $\Delta$ 2-1,2,4-thiadiazoline-5-one hydrazone,  
 1,4-dimethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 1,4-dihydroxyethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,  
 30 1,4-diaminoethyl- $\Delta$ 2-1,2,4-triazoline-5-one hydrazone,

1,3,4-trimethyl- $\Delta^2$ -1,2,4-triazoline-5-one hydrazone,  
1,4-dimethyl-3-phenyl- $\Delta^2$ -1,2,4-triazoline-5-one hydrazone and  
4-methyl-3-phenyl- $\Delta^2$ -1,2,4-triazoline-5-one hydrazone.

- 5 Among the compounds of formula (I), the following thiazolone hydrazone derivatives and the salts thereof are particularly preferred:
- 3-methyl-2(3H)thiazolone hydrazone,  
3,4-dimethyl-2(3H)thiazolone hydrazone,  
4-tert.butyl-3-methyl-2(3H)thiazolone hydrazone,  
10 3-methyl-4-phenyl-2(3H)thiazolone hydrazone,  
3-methyl-4-(4-tolyl)-2(3H)-thiazolone hydrazone,  
4-(4-methoxy)phenyl-3-methyl-2(3H)-thiazolone hydrazone,  
4-(4-ethoxy)phenyl-3-methyl-2(3H)-thiazolone hydrazone,  
4-(4-bromophenyl)-3-methyl-2(3H)-thiazolone hydrazone,  
15 4-(3-bromophenyl)-3-methyl-2(3H)-thiazolone hydrazone,  
4-(4-chlorophenyl)-3-methyl-2(3H)-thiazolone hydrazone,  
4-(3-chlorophenyl)-3-methyl-2(3H)-thiazolone hydrazone,  
3-methyl-4-(4-nitrophenyl)-2(3H)-thiazolone hydrazone,  
3-methyl-4-(3-nitrophenyl)-2(3H)thiazolone hydrazone,  
20 4-[(1,1'-biphenyl)-4-yl]-3-methyl-2(3H)-thiazolone hydrazone,  
ethyl 2-hydrazono-2,3-dihydro-3-methyl-4-thiazolecarboxylate,  
3,4,5-trimethyl-2(3H)-thiazolone hydrazone,  
3,4-dimethyl-5-phenyl-2(3H)-thiazolone hydrazone,  
3,5-dimethyl-4-phenyl-2(3H)-thiazolone hydrazone,  
25 4,5-diphenyl-3-methyl-2(3H)-thiazolone hydrazone,  
5-ethyl-3-methyl-4-phenyl-2(3H)-thiazolone hydrazone,  
4-(4-bromophenyl)-3-methyl-5-phenyl-2(3H)-thiazolone hydrazone,  
3-methyl-5-phenyl-4-(4-tolyl)-2(3H)-thiazolone hydrazone,  
5-(4-chlorophenyl)-4-phenyl-3-methyl-2(3H)-thiazolone hydrazone,  
30 5-(4-chlorophenyl)-4-(4-methoxyphenyl)-3-methyl-2(3H)-thiazolone hydrazone,

ethyl 2-hydrazono-2,3-dihydro-3,4-dimethyl-4-thiazolecarboxylate,  
 4-amino-2-hydrazino-2,3-dihydro-3-methyl-5-thiazole carbonitrile  
 4,5-dimethyl-3-ethyl-2(3H)-thiazolone hydrazone,  
 ethyl 2-hydrazono-2,3-dihydro-3-ethyl-4-methylthiazolecarboxylate,  
 5 5-methyl-3-(1-methylethyl)-4-phenyl-2(3H)-thiazolone hydrazone,  
 4,5-diphenyl-3-(1-methylethyl)-2(3H)-thiazolone hydrazone  
 4,5-diphenyl-3-propyl-2(3H)-thiazolone hydrazone,  
 3-butyl-4,5-diphenyl-2(3H)-thiazolone hydrazone,  
 4,5-diphenyl-3-(2-methylpropyl)-2(3H)-thiazolone hydrazone,  
 10 3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4-methyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4-tert.butyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4-phenyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 4,5-diphenyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,  
 15 3-hydroxyethyl-2(3H)-thiazolone hydrazone,  
 3-hydroxyethyl-4-methyl-2(3H)-thiazolone hydrazone,  
 3-aminoethyl-2(3H)-thiazolone hydrazone,  
 3-aminoethyl-4-methyl-2(3H)-thiazolone hydrazone,  
 3-phenyl-2(3H)-thiazolone hydrazone,  
 20 4-methyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 3,4-diphenyl-2(3H)-thiazolone hydrazone,  
 4-p-biphenyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 4-(4-methoxy)phenyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 4-tert.butyl-3-phenyl-2(3H)-thiazolone hydrazone,  
 25 3,4-diphenyl-5-methyl-2(3H)-thiazolone hydrazone,  
 3,4,5-triphenyl-2(3H)-thiazolone hydrazone,  
 4,5-dimethyl-3-(phenylmethyl)-2(3H)-thiazolone hydrazone,  
 ethyl 2-hydrazono-2,3-dihydro-3-[(phenylamino)carbonyl]-4-methylthiazolecarboxylate  
 3-methyl-4,5,6,7-tetrahydro-2(3H)-benzothiazolone hydrazone,  
 30 3-methyl-2(3H)benzothiazolone hydrazone,

3,6-dimethyl-2(3H)benzothiazolone hydrazone,  
 6-chloro-3-methyl-2(3H)benzothiazolone hydrazone,  
 7-chloro-3-methyl-2(3H)benzothiazolone hydrazone,  
 6-hydroxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 5 5-methoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 7-methoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 5,6-dimethoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 5-ethoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 6-ethoxy-3-methyl-2(3H)benzothiazolone hydrazone,  
 10 3-methyl-5-nitro-2(3H)benzothiazolone hydrazone,  
 3-methyl-6-nitro-2(3H)benzothiazolone hydrazone,  
 5-acetamido-3-methyl-2(3H)benzothiazolone hydrazone,  
 6-acetamido-3-methyl-2(3H)benzothiazolone hydrazone,  
 5-anilino-3-methyl-2(3H)benzothiazolone hydrazone,  
 15 6-anilino-3-methyl-2(3H)benzothiazolone hydrazone,  
 2-hydrazono-2,3-dihydro-3-methyl-6-benzothiazolecarboxylic acid,  
 2-hydrazono-2,3-dihydro-3-methyl-4-benzothiazolesulfonic acid,  
 2-hydrazono-2,3-dihydro-3-methyl-5-benzothiazolesulfonic acid,  
 2-hydrazono-2,3-dihydro-3-methyl-6-benzothiazolesulfonic acid,  
 20 2-hydrazono-2,3-dihydro-3-methyl-7-benzothiazolesulfonic acid,  
 2-hydrazono-2,3-dihydro-N,N,3-trimethyl-6-benzothiazolesulfonamide,  
 [(2-hydrazono-2,3-dihydro-3-methyl-6-benzothiazolyl)oxy]acetic acid hydrazide,  
 3-methylnaphtho[2,3-d]thiazol-2(3H)one hydrazone  
 3-ethyl-2(3H)benzothiazolone hydrazone,  
 25 6-ethoxy-3-ethyl-2(3H)benzothiazolone hydrazone,  
 3-propyl-2(3H)benzothiazolone hydrazone,  
 3-butyl-2(3H)benzothiazolone hydrazone,  
 3-hexyl-2(3H)benzothiazolone hydrazone,  
 3-hydroxyethyl-2(3H)benzothiazolone hydrazone,  
 30 3-aminoethyl-2(3H)benzothiazolone hydrazone,

3-p-methylbenzyl-2(3H)benzothiazolone hydrazone,  
2,3-dihydro-2-hydrazono-3-(2-hydroxyethyl)-6-benzothiazolecarboxylic acid  
2,3-dihydro-2-hydrazono-6-methoxy-3(2H)benzothiazolepropanesulfonic acid,  
6-hexadecyloxy-2-hydrazono-3(2H)benzothiazolepropanesulfonic acid,  
5 ethyl 2-keto-3-benzothiazolineacetate hydrazone,  
3-acetyl-2(3H)benzothiazolone hydrazone and  
2-hydrazono-3(2H)benzothiazole carboxaldehyde.

10 Some compounds of formula (I) are commercially available, but they can also be prepared by methods of synthesis known from the literature, for example by the method described in Research Disclosure 174, pp. 42-44 (1978) or in analogy with the method described in DE-A 1 049 381.

15 Suitable CH-active compounds of general formulas (II) to (IX) are, in particular, the following compounds and the salts thereof:  
cyanoacetic acid, methyl cyanoacetate, ethyl cyanoacetate, malonic acid dinitrile, pivaloylaceto-nitrile, 2-cyanoacetamide, 2-cyano-1-methyl-4-nitrobenzene, barbituric acid,  
20 thiobarbituric acid, 1,3-dimethylthiobarbituric acid, 1-methyl-1,2-dihydro-6-hydroxy-4-methyl-2-ketopyridine-3-carbonitrile, 1-ethyl-1,2-dihydro-6-hydroxy-4-methyl-2-ketopyridine-3-carbonitrile, 1-hydroxyethyl-1,2-dihydro-6-hydroxy-4-methyl-2-ketopyridine-3-carbonitrile, 1,3-dihydro-2H-indol-2-one, benzofuran-3(2H)-one,  
2-phenyl-3,5-dihydroimidazol-4-one, 3-indoxyl acetate, 2-thioxo-4-thiazolidinone and 4-  
25 keto-2-thioxo-3-thiazolidinylacetic acid, among which the following compounds are particularly preferred: cyanoacetic acid, methyl cyanoacetate, ethyl cyanoacetate, malonic acid dinitrile, barbituric acid, thiobarbituric acid, 1,3-dimethylthiobarbituric acid, 1,3-dihydro-2H-indol-2-one, 2-thioxo-4-thiazolidinone and 4-keto-2-thioxo-3-thiazolidinylacetic acid.

30

The colorants of the invention are used in conjunction with an oxidant. Suitable oxidants are those usually employed in hair colorants, for example hydrogen peroxide or the addition compounds thereof, persalts such as the persulfate salts and perborate salts, or peracids and enzymatic oxidation systems. Air oxidation is also feasible. Preferred

5 oxidants are hydrogen peroxide or the addition compounds thereof (for example sodium percarbonate, urea peroxide etc) and the persalts such as the persulfate salts or perborate salts, for example potassium persulfate, sodium persulfate or ammonium persulfate, as well as mixtures thereof.

10 The oxidants are contained in the ready-to-use colorant (A) in a total amount from about 0.01 to 10 weight percent and preferably from about 0.1 to 5 weight percent.

Moreover, besides the compounds of formula (I) and compounds of formulas (II) to (IX), the colorant of the invention can also contain other common, physiologically

15 unobjectionable direct dyes from the group of cationic and anionic dyes, disperse dyes, azo dyes, quinone dyes and triphenylmethane dyes. The direct dyes are contained in the ready-to-use colorant (A) in an amount from about 0.01 to 10 weight percent and preferably from about 0.1 to 5 weight percent.

20 Each of the compounds of formula (I) and of the compounds of formulas (II) to (IX) is contained in the ready-to-use colorant (A) in a total amount from about 0.01 to 10 weight percent and preferably from about 0.1 to 5 weight percent.

As a rule, the compounds of formula (I) and the compounds of formulas (II) to (IX) are

25 stored separately from one another and are mixed with the oxidant only just before use. It is also possible, however, provided the compounds of formula (I), the compounds of formulas (II) to (IX) and the oxidant are solids, to package them together and to obtain the ready-to-use colorant (A) just before use by mixing the compounds of formula (I), the compounds of formulas (II) to (IX) and the oxidant with water or with a liquid preparation

30 containing the other components of the colorant. It is also possible, provided the



compounds of formula (I) and the compounds of formulas (II) to (IX) are solids, to package them together and to prepare the ready-to-use colorant (A) by mixing the compounds of formula (I) and the compounds of formulas (II) to (IX) with the oxidant just before use.

5

The colorant of the invention thus as a rule consists of several components that are mixed with one another just before use. Preferably, the colorant is provided as a 2-component kit consisting of dye carrier composition (A1) containing the compounds of formula (I) and an additional dye carrier composition (A2) containing the compounds of formulas (II) to (IX) and optionally an oxidant, or it is provided as a 3-component kit consisting of a dye carrier composition (A1) containing the compounds of formula (I), another dye carrier composition (A2) containing the compounds of formulas (II) to (IX) and a third component (A3) containing an oxidant.

10  
15 Particularly preferred is a 3-component kit consisting of a dye carrier composition (A1) containing the compounds of formula (I), another dye carrier composition (A2) containing the compounds of formulas (II) to (IX) and a third component (A3) containing an oxidant.

Another object of the present invention is a multicomponent kit consisting of a preparation of component (A1) and a preparation of component (A2), the oxidant possibly being packaged as component (A3) separately from component (A2), and optionally of an agent for adjusting the pH (an alkalinizing agent or an acid). Naturally, the preparations of components (A1) and (A2) can consist of several individual components that are mixed with one another just before use. Another possibility is a 2-component kit of which the 1st component consists of a powder containing the compounds of formula (I), the compounds of formulas (II) to (IX) and optionally an oxidant, provided the compounds of formula (I), the compounds of formulas (II) to (IX) and the oxidant are solids, and optionally other common powdered cosmetic additives, and the 2nd component of which is water or a liquid cosmetic preparation. Preferred is a 2-component kit of which the 1st component consists of a powder containing the compounds of formula (I), the compounds of formulas

(II) to (IX) and the oxidant and optionally other common powdered cosmetic additives, and the 2nd component of which is water or a liquid cosmetic preparation.

The components (A1) and (A2) and ready-to-use colorant (A) are provided, for example, as a solution, particularly an aqueous or aqueous-alcoholic solution, a cream, a gel or an emulsion. Their composition consists of a mixture of the compound of formula (I) or compound of formulas (II) to (IX) and optionally of an oxidant, with the additives normally used for such preparations.

Commonly used additives to solutions, creams, emulsions, gels or aerosol foams are, for example, solvents such as water, the lower aliphatic alcohols, for example ethanol, n-propanol and isopropanol, or glycols such as glycerol and 1,2-propanediol, furthermore wetting agents or emulsifiers from the classes of anionic, cationic, amphoteric or nonionic surface-active substances, such as the fatty alcohol sulfates, ethoxylated fatty alcohol sulfates, alkyl sulfonates, alkyl benzenesulfonates, alkyltrimethylammonium salts, alkylbetaines, ethoxylated fatty alcohols, ethoxylated nonylphenols, fatty alkanolamides, ethoxylated fatty esters, furthermore thickeners such as the higher fatty alcohols, starch or cellulose derivatives, perfumes, hair pretreatment agents, conditioners, hair-swelling agents, preservatives, furthermore vaselines, paraffin oil and fatty acids and also hair-care agents such as cationic resins, lanolin derivatives, cholesterol, pantothenic acid and betaine. The said constituents are used in amounts usually employed for such purposes, for example the wetting agents and emulsifiers at a concentration of about 0.5 to 30 weight percent [in all cases based on component (A1) or (A2)], the thickeners in an amount of about 0.1 to 25 weight percent [in all cases based on component (A1) or (A2)] and the hair-care agents at a concentration of about 0.1 to 5.0 weight percent [in all cases based on component (A1) or (A2)].

The pH of the ready-to-use colorant (A) is in all cases about 6 to 12 and preferably about 7 to 11. The ready-to-use colorant (A) is adjusted to the pH desired for the coloring by addition of an alkalinizing agent, for example ammonia, an amino acid, alkanolamine, alkali metal hydroxide, alkaline earth metal hydroxide, alkali metal acetate, alkaline earth

metal acetate, ammonium carbonate, alkali metal carbonate, alkaline earth metal carbonate, alkali metal silicate, alkaline earth metal silicate or ammonium silicate, or by addition of an acid, for example lactic acid, acetic acid, tartaric acid, phosphoric acid, hydrochloric acid, citric acid, ascorbic acid or boric acid.

5

The ready-to-use colorant is prepared just before use by mixing components (A1) and (A2) or (A1), (A2) and (A3), optionally with addition of an alkalinizing agent or an acid, and is then applied to the fibers, particularly human hair. Depending on the color depth desired, this mixture is allowed to act for about 5 to 60 minutes, preferably about 15 to 30 minutes, at a temperature of about 20 to 50 °C and particularly about 30 to 40 °C. The fibers are then rinsed with water, optionally washed with a shampoo and dried.

10

The colorant of the invention imparts to the fibers, particularly keratin fibers, for example human hair, a uniform, intense, brilliant and lasting coloration.

15

The following examples will provide a more detailed explanation of the subject matter without limiting it to these examples.

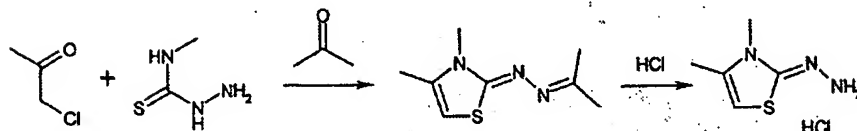
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## EXAMPLES

30

**Example 1:                      Synthesis of 3,4-dimethyl-2(3H)thiazolone  
hydrazone hydrochloride**



5    **Step A: 3,4-Dimethyl-2(3H)thiazolone-(1-methylethylidene) hydrazone**

21 g (200 mmol) of 4-methyl-3-thiosemicarbazide in 1000 mL of acetone was heated at reflux for 2 hours. To this solution was then added dropwise 20.4 g (220 mmol) of chloroacetone. The reaction mixture was allowed to reflux for 7 hours and was then  
10 concentrated. The resulting crude product was recrystallized from acetone. This gave 23 g of an orange-colored powder (63% of the theoretical).

Melting point: 139-139.6 °C

<sup>1</sup>H-NMR (DMSO, 300 MHz): δ = 6.72 [s, broad, 1H, H-C(5)]; δ = 3.67 (s, 3H, N-CH<sub>3</sub>); δ = 2.27 [d, J = 0.9 Hz, 3H, CH<sub>3</sub>-C(4)]; δ = 2.17 (s, 3H, CH<sub>3</sub>); δ = 2.07 (s, 3H, CH<sub>3</sub>)

15 <sup>13</sup>C-NMR (DMSO, 300 MHz): δ = 169.16; 164.14; 139.02 [C(4)]; 103.36 [C(5)]; 34.47 (CH<sub>3</sub>N); 24.60; 19.91; 13.53 [CH<sub>3</sub>(C4)].

MS (ESI): 184 (M<sup>+</sup> + 1)

**Step B: 3,4-Dimethyl-2(3H)thiazolone hydrazone hydrochloride**

20 3.5 g (19 mmol) of 3,4-dimethyl-2(3H)thiazolone-(1-methylethylidene) hydrazone from step A in 60 mL of 6M hydrochloric acid was heated at 50 °C for 30 minutes. The reaction mixture was then concentrated, and the crude product was recrystallized from ethanol. This gave 2 g (60% of the theoretical) of a pink-colored powder.

25 Melting point: 156.4 -156.6 °C

<sup>1</sup>H-NMR (DMSO, 300 MHz): δ = 6.58 [q, J = 0.9 Hz, 1H, H-C(5)]; δ = 3.41 (s, 3H, N-CH<sub>3</sub>); δ = 2.18 [d, 0.9 Hz, 3H, CH<sub>3</sub>-C(4)].

MS (ESI): 144 ( $M^+ + 1$ ).

$^{13}\text{C}$ -NMR (DMSO, 300 MHz):  $\delta$  = 172.30 [C(2)]; 138.79 [C(4)]; 101.43 [C(5)]; 32.92 ( $\text{CH}_3\text{N}$ ); 13.40 [ $\text{CH}_3(\text{C4})$ ];

CHN analysis:  $[\text{C}_5\text{H}_9\text{N}_3\text{S} (0.96 \text{ HCl})(0.5 \text{ EtOH})]$ :

	%C	%H	%N	%S	%Cl
Calculated:	35.81	6.49	20.88	15.93	16.90
Found:	35.20	6.30	21.00	15.40	16.80

**Examples 2-6: Colorants with 3,4-dimethyl-2(3H)thiazolone  
hydrazone hydrochloride**

Component (A1)

4.00 g	of decylpolyglucose, 50% aqueous solution
0.20 g	of disodium ethylenediaminetetraacetate hydrate
5.00 g	of ethanol
0.45 g	of 3,4-dimethyl-2(3H)thiazolone hydrazone hydrochloride
to 100.00 g	water, demineralized

Component (A2)

Y g	of CH-active compound as per Table 1
0.40 g	of potassium persulfate

The foregoing constituents were mixed uniformly with one another at room temperature (20-25 °C) or with slight heating (35-40 °C). The pH of the ready-to-use colorant (A) was adjusted to the value given in Table 1 with sodium hydroxide solution, sodium carbonate or ammonia.

The ready-to-use colorant was applied to bleached hair and uniformly distributed with a brush. After an exposure time of 30 min at 40 °C, the hair was rinsed with lukewarm water, washed with a commercial shampoo, rinsed with lukewarm water and then dried.

The amount of CH-active compound of formulas (II) to (IX) used and the resulting colorations are collected in the following Table 1.

5

**Table 1**

Example No.	CH-Active Compound Used, (Amount in g)	pH	Coloration
2	thiobarbituric acid (0.36 g)	9.3	yellow
3	1,3-dihydro-2H-indol-2-one (0.33 g)	9.8	yellow
4	2-thioxo-4-thiazolidinone (0.33 g)	9.2	orange
5	ethyl cyanoacetate (0.28 g)	9.7	yellow-green
6	malonic acid dinitrile (0.17 g)	9.1	golden-yellow

10 **Examples 7 + 8: Colorants with 3-Methyl-2(3H)-benzothiazolone hydrazone hydrochloride**

Component (A1)

15        4.00 g        of decylpolyglucose, 50% aqueous solution  
           0.20 g        of disodium ethylenediaminetetraacetate hydrate  
           5.00 g        of ethanol  
           0.58 g        of 3-methyl-2(3H)-benzothiazolone hydrazone hydrochloride hydrate  
           to 100.00 g    demineralized water

20

Component (A2)

Y g        of CH-active compound as per Table 2